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SEALING CERAMIC MATERIAL IN LOW MELTING POINT GLASS

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16. Abstract This is an invention of a structured device placed in an aera- ted crucible to pack ceramics molding substance that is to be processed. The structure is wrapped by sealing material made of pyrex glass and graphite foil or sheet that has a weight attached on top of it. The crucible is made of carbon; the ceramics material to be treated through heat intervenient press process is molding substance consisting mainly of silicon nitride.					
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1. Name of the invention

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Sealing ceramic material in low melting point glass.

2. Scope of the patent application

(1) The structured device placed in an aerated crucible to pack ceramic molding substance which is to be processed by the heat intervenient press. The entire device is covered by sealing material made of glass and graphite foil or sheet that has a weight attached on top of it.

(2) The packing device for molding substance to be treated described in para 2 (1) of which the aerated crucible is made of carbon.

(3) The packing device for molding substance to be treated described in para 2 (1) and (2) of which the ceramics substance to be treated is molding substance consisting mainly of silicon nitride.

(4) The packing device for molding substance to be treated described in para 2 (1), (2) and (3) of which surface is surrounded by the top and the bottom glass plate and glass granules in between.

(5) The packing device for molding substance to be treated described in para 2 (1) and (4) of which the glass is pyrex glass.

3. Detailed description of the invention

This invention is in regard to the structured packing

*Numbers in the margin indicate pagination in the foreign text.

device for molding substance to be treated by the heat intervenient press. To be precise, it is the device that uses a glass seal made of liquefied glass as the sealing material for ceramic molding substance in the process of the heat intervenient press.

The heat intervenient press (hereinafter referred to as HIP) method that uses glass as the sealing material has several advantages - molding of a variety of forms and shapes is possible; high temperature HIP is possible, in contrast with copper, which is commonly used as capsule material. Its application in high density ceramics of which development is being pushed forward these days is being attempted. For example, the glass capsule method (Ref. to Kokai Patent No. 46-2731), and the method to imbed molding substance in glass granules (Ref. to Kokai Patent No. 55-89405) are some of the examples. /416

These methods all use crucibles made of carbon such as graphite, and it surrounds the molding substance by melting glass within the crucible. Because ceramics powder has a high sintering temperature requiring high HIP temperature compared to metal powder molding of the past, glass is used to process ceramics such as silicon nitride and silicon carbide. At this time, ceramics molding substance, regardless of the method - glass sealing method as mentioned earlier or glass powder imbedding method - used, become imbedded in the mass of glass. However, because the specific gravity of ceramics molding substance until it becomes high density substance is lower ($1.8 - 2.1 \text{ g/m}^3$) than that of glass ($2.2 - 2.3 \text{ g/m}^3$), molding substance tends to surface from its original position and contact the surface of the carbon crucible

when the glass dissolves.

In this instance, gas used as pressuring medium enters the crucible from the contact point during the process of HIP resulting in imperfect sealing, which causes incomplete HIP. In addition, a very small amount of oxygen contained in gas used as a medium causes chemical reactions with ceramics. Also, even if BN powder is used to promote smooth separation of the carbon crucible and molding substance, solidified glass is difficult to remove from the carbon crucible.

In spite of the shortcomings of glass as mentioned above, its use is industrially advantageous due to its low cost and ease in handling. Therefore, improvement of the shortcomings is hoped for.

This invention, meeting the needs of the time, aims to provide an improved packing device with an improved sealing structure that can effectively provide sealing by glass with a low melting temperature.

The characteristics of this invention, which is capable of attaining the above mentioned aims, are : (1) the device packs glass sealing material by surrounding the molding substance placed in the molding substance packing crucible inserted in the HIP device, (2) the device surrounds the molding substance and glass sealing material with an airproof graphite sheet, while a free moving weight is placed on top.

The following are more detailed explanation of this invention with figures:

The figure is one example of the structure by this

invention. Molding substance (2) is packed surrounded by the top and the bottom glass plates (3) (3') and glass granule (4) in between. Next to the molding substance (2) and glass (3)(3')(4) is an airproof sheet of graphite (5), a main part of this invention. On top of the graphite sheet (5) is a free moving weight which prevents the molding substance (2) from surfacing at the time of HIP.

The crucible (1) is air-permeable, usually made of carbon, so that Ar, N₂ and other pressure media gases may go through.

On the other hand, the molding substance (2) includes all material that are processed by HIP, eg. metallic or ceramics powder. Among molding substance, ceramic substance, with glass as sealing material, is the most suitable for the high temperature process of HIP. Among them, the most favorable ones are ceramics substance composed mainly of silicon nitride, silicon carbide and boron carbide. Also, the molding substance (2) is not just an ordinary powder - it sometimes contains sintering promoting agent, and it is sometimes in the form of preparatory sintering substance.

As for glass to be used for sealing, any glass commonly used for HIP process, eg. silica glass, pyrex glass...etc., can be used. Among those commonly used, pyrex glass is the most favorable because of its characteristics during and after HIP process - no reaction with ceramics and easily removable after HIP. According to the figure, the structure for the sealing glass consists of the top, bottom plates and in-between glass granules, but the formation does not have to be followed strictly. The structure can be

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modified to suit the need. Glass granule alone may be used sometimes, and molding substance may be placed in a glass capsule. Also, in addition to plate and granule forms of glass, other forms can be used effectively.

The air-proof graphite sheet prevents gases through the crucible (1) from entering during HIP process as well as conveying even compression force to molding substance (2). It is required to be air-proof as well as dissolution-proof at the high temperature of HIP processing.

Among possible materials that can satisfy the above requirement are graphite, molybdenum and other metals of high dissolution points. All except graphite are unacceptable due mainly to their costs. The most suitable one is graphite product named grafoil (a trade name) which possesses all the necessary qualities mentioned earlier.

On top of the glass sheet (5) is a weight (6) which prevents the molding substance (2) from surfacing when the glass is dissolved. It is made of material suitable for usage in high temperature, and has enough weight to prevent the molding substance which has less specific gravity than glass from surfacing. The suitable material for the weight are silicon nitride, tungsten, molybdenum and others. The weight (6) needs to be movable in order that changes of shapes and forms of material below during the process do not affect the up and down movement of the weight along the inner wall of the crucible.

In the figure, (7) indicates a layer of BN powder applied on the inner surface of the crucible. Although it is not

indispensable for an easy removal of molding substance from the crucible, it is effective in the same manner as the graphite sheet after the process.

The packing structure for molding substance thus far, used in HIP process with Ar and N₂ used as pressure media gas, and inserted in the crucible in its original form. In case pyrex glass is used, the glass starts to dissolve at 1200 degrees C; molding substance not yet in high density form starts to surface due to its low specific gravity and pushes up the graphite sheet placed above it; a portion of molding substance within glass sealing begins to surface.

However, because of the weight (6) placed on top, the surfacing of the substance as well as the entry of pressure media gases are kept off, thus, complete sealing is maintained. Gases released from molding substance during the early stage of HIP flow between the glass because the glass seal is not completed.

After the glass has dissolved, the gases are dissolved in glass (a characteristic of pyrex glass); molding substance can attain the desired high density under the designated HIP temperature and pressure level. The gases dissolved in the glass are re-vaporized making the glass foam, which is ideal for removal of glass after the process.

As described thus far, the packing structure for molding substance by this invention surrounds molding substance with an air-proof graphite sheet, and prevents pressure media gases from entering the area of molding substance by a weight placed on top of the molding substance. In addition, the long standing problem

associated with HIP - surfacing of molding substance during HIP - can be effectively solved by the weight which pushes down molding substance and provides a complete sealing.

Moreover, the graphite sheet by this invention does not prevent molding substance from changing itself to high density substance; solidified glass after HIP can be removed from the crucible easily because of the effect of the graphite sheet. Above all, most importantly, the graphite sheet prevents pressure media gases from mixing with molding substance - the basic principle of HIP. The following is an example of a practical application:

Powder form of Si_3N_4 , purity 99%, α element 70%, average diameter 1 micron, was placed in a tube made of silicon rubber; 5000 Kg/cm pressure was evenly applied to form a preparatory molding substance (18 mm ϕ x 30 mm l).

The preparatory molding substance was placed in a graphite crucible of which the inner surface was coated with BN. The preparatory molding substance was placed between two sheets of pyrex glasses, one at the top and one at the bottom. Pyrex glass granules were filled in the space between the two glass plates. The preparatory molding substance and glasses were wrapped by graphite foil; a weight was placed on top of the substance. After these preparations, the preparatory molding substance was placed in a HIP device where HIP process was started at 300 degrees C temperature at the beginning. After decompression down to 10 Torr, two exhaustion operations by injecting N_2 gas, 15 Kg/cm². The temperature was raised to 1200 degrees C until the glass was dissolved; N_2 gas was re-supplied and the temperature was raised

again, and HIP process was continued for two hours at 1750 degrees C temperature and 2000 Kg f/cm² .

The molding substance taken out of the HIP device, covered with dark glass substance, was completely free of media gases on the surface of Si₃N₄, and its relative density was 98.5 %.

4. Brief explanation of the figure

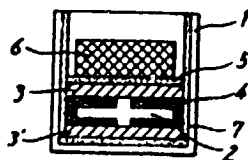
The figure indicates one example of the packing structure of the molding substance by this invention.

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KEY LIST

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|----------------------------|-----------------------|
| (1) crucible | (2) molding substance |
| (3)(3') glass plate | (4) glass granules |
| (5) graphite foil or sheet | (6) weight |
| (7) a layer of BN agent | |



ORIGINAL FIGURE
OF POOR QUALITY